Your reference 30677/G1000{PRIVATE }

(19) JAPAN PATENT BUREAU (JP)

(11) Publication No.: 2003-73602
(P2003-73602A)

(12) OFFICIAL GAZETTE LAID-OPEN PATENT (A)

(43) Date of laying open: 3/12/2003

(51) Int. Cl.[7]:	ID Code:	FI:		Theme code (ref.)
C 09 D 11/16		C09D 11/16		2 C 3 5 0
B 43 K 7/00		B43K 7/00		4 J 0 3 9
8/02		8/02	A	
			F	

Request for exam.: None No. of Claims: 6 OL (Total of 6 pages)

{PRIVATE }(21) Application No.: 2001-270576
(P2001-270576)

(22) Date of Application: 9/6/2001

(71) Applicant: 000108328
ZEBRA K. K.
2-9, Higashi Gokencho,
Shintuku-ku, Tokyo-to

(72) Inventor: T. YUE
c/o Zebra K.K.
2-9, Higashi Gokencho,
Shintuku-ku, Tokyo-to

(72) Inventor: N. SAKURAI
c/o Zebra K.K.
2-9, Higashi Gokencho,
Shintuku-ku, Tokyo-to

(74) Agent: 100109955
S. HOSOE, Patent Agent
(and 2 others)

Continued on the last page.

(54) Title: WATER-BASED INK FOR A WRITING IMPLEMENT AND A WRITING IMPLEMENT FILLED WITH THE SAME

(57) **Abstract:**

Issues:

To offer water-based ink for a writing implement, the traced part of which changes color when the written line is traced with a color-changing writing implement filled with a color-changing liquid of sulfurous-acid-based reducing agent, and a writing implement filled with such water-based ink.

Solution means:

Water-based ink for a writing implement that contains at least both a basic dyes, erasable with a sulfurous-acid-based reducing agent, and a color agent non-erasable with the reducing agent, and a writing implement filled with the said water-based ink.

PATENT CLAIMS

Claim 1:

Water-based ink for a writing implement that contains at least a basic dye erasable with a sulfurous acid reducing agent and a coloring agent non-erasable with a sulfurous acid reducing agent.

Claim 2:

Water-based ink of Claim 1 that contains 0.1-10 weight % of basic dye erasable with a sulfurous acid reducing agent and 0.1-10 weight % of coloring agent non-erasable with a sulfurous acid reducing agent.

Claim 3:

Writing implement filled with the water-based ink of Claim 1 or Claim 2.

Claim 4:

Writing implement characterized by the paired use of a writing implement filled with the water-based ink of Claim 3 and a writing implement filled with a color-changing fluid that contains a sulfurous acid reducing agent that erases the basic dye contained in the water-based ink filled in the said writing implement.

Claim 5:

Writing implement of Claim 4 in which the color-changing fluid does not contain a coloring agent.

Claim 6:

Writing implement of Claim 4 in which the color-changing fluid contains a coloring agent.

DETAILED EXPLANATION

[0001]

Area of technology of the invention:

This invention relates to a water-based ink used in a writing implement, such as a ballpoint pen or marker pen, etc., and a writing implement filled with the said water-based ink and, further in detail, it relates to the water-based ink, the written line of which is discolored when it is traced with a color-changing writing implement filled with a color-changing fluid and it relates to a writing implement filled with the said water-based ink.

[0002]

Conventional technology:

Conventionally, Patent S54-22344 discloses an ink for writing that erases the once written line. This writing ink uses a specific basic dye as its coloring agent and the color of the written line, written with the said writing ink is erased when the line is traced (written over) by a fluid that contains a sulfurous acid reducing agent. However, even when a specific part of the letter written with the said writing ink is not to be erased, such objective cannot be achieved unless a writing implement, filled with normal writing ink that contains a coloring agent of general use, is used for writing.

[0003]

Problem to be solved:

Therefore, the purpose of this invention is to offer a water-based ink, the once written line of which discolors but cannot be erased when it is traced, and a writing implement filled with the said writing water-based ink.

[0004]

Solution means:

In order to achieve the said objective, the water-based ink of this invention contains at least one basic dye erasable with a sulfurous acid reducing agent and a coloring agent not erasable with a sulfurous acid reducing agent. In this case, 0.1-10 weight % compounding of a basic dye, which is erasable with a sulfurous acid reducing agent in the water-based ink is preferable and 0.1-10 weight % compounding of a coloring agent, which is non-erasable with a sulfurous acid reducing agent is preferable. Also, in this invention, for achievement of the said objective, a writing implement filled with the said water-based ink and a color-changing writing implement filled with a color-changing fluid that contains a sulfurous acid reducing agent that erases the basic dye contained in the water-based ink, are used as a pair. In this case, the said color-changing fluid either contains a coloring agent or does not contain it.

[0005]

A line written with a writing implement such as a ballpoint pen or marker pen, etc., filled with the said water-based ink, has the color which results when the color of the basic dye, erasable with a sulfurous acid reducing agent, and the color of the coloring agent, not erasable with a sulfurous acid reducing agent, are mixed in the beginning of the writing. When the color-changing writing implement filled with a color-changing fluid containing a sulfurous acid reducing agent is used to trace the written line, the basic dye is reduced by the sulfurous acid reducing agent and its color is erased, while the color of the coloring agent not erasable with a sulfurous acid reducing agent remains, so that the color of the traced written line is changed.

[0006]

Practical Example:

The preferred mode of this invention is detailed below.

The water-based ink of this invention contains at least a basic dye erasable with a sulfurous acid reducing agent and the coloring agent not erasable with a sulfurous acid reducing agent and ion-exchanged water is added to it.

[0007]

The basic dye, erasable with a sulfurous acid reducing agent, can be, for example, Basic Orange 21, C.I. Basic Red 13, ditto 14, C.I. Basic Blue 3, ditto 54, C.I. Basic Green 1, etc., given with the color index number (C.I. hereafter). These dyes can be used alone or in a mixture, depending on the color and tone required. Compounding 0.1-10 weight % of a basic dye erasable with a sulfurous acid reducing agent in the water-based ink of this invention is preferred. When this is less than 0.1 weight %, the darkness of the written line is low and when it is more than 10 weight %, it does not dissolve in the water-based ink and it can precipitate or it increase the viscosity of the ink.

[0008]

The coloring agent not erasable with a sulfurous acid reducing agent can be a basic dye and pigment other than the abovementioned basic dye that is erasable with a sulfurous acid reducing agent. However, an acidic dye or direct dye reacts with the basic dye erasable with a sulfurous acid reducing agent and precipitates, so these cannot be used. The basic dye that can be used as the basic dye not erasable with a sulfurous acid reducing agent can be, for example, C.I.

Basic Yellow 11, Basic Yellow 21, C. I. Basic Red 1, Basic Red 18, C.I. Basic Blue 7, Basic Blue 65, etc. The pigment that can be used as the coloring agent not erasable with a sulfurous acid reducing agent can be, for example, an organic pigment having an azo group, phthalocyanine group, quinacridine group, dioxazine group, etc. or an inorganic pigment such as titanium oxide or metal powder, etc. These coloring agents not erasable with a sulfurous acid reducing agent, can also be used singly or as a mixture of two or more. The 0.1-10 weight % compounding of the coloring agent not erasable with a sulfurous acid reducing agent in the water-based ink is preferable. When it is less than 0.1 weight %, the darkness of the written line is low and when it is more than 10 weight %, it increases the viscosity of the ink.

[0009]

The water-based ink of this invention contains water (ion-exchanged water) similarly to the conventional one and 50-90 weight % compounding is preferable. In addition, an additive, such as a gelling agent, thickener, antiseptic, water-soluble organic solvent, anticorrosion agent, dye dissolution assisting agent, pH adjuster, fixing resin, surfactant, etc., can be added, if needed.

[0010]

The water-based ink of this invention is stored in a writing implement by a means similar to the conventional, in a ballpoint pen or marker pen, and it is discharged from the nib.

[0011]

Next, the writing implement of this invention is explained in detail.

A writing implement filled with the water-based ink of this invention and a writing implement filled with a color-changing fluid that contains a sulfurous acid reducing agent that erases the basic dye of the water-based ink are used as a pair in this invention. That is, the color-changing fluid containing a sulfurous acid reducing agent is used to trace over a line written by the writing implement filled with water-based ink that contains at least a coloring agent not erasable with a sulfurous acid reducing agent and the basic dye erasable with a sulfurous acid reducing agent in order to change the color of the written line. Here, the color-changing fluid is a fluid that can change the color of the written line when it is traced over the written line written by the writing implement filled with the said water-based ink.

[0012]

The color-changing fluid that changes the color of a line written by the writing implement filled with the water-based ink of this invention, by tracing the implement over the written line, contains at least one sulfurous acid reducing agent. The sulfurous acid reducing agent can be, for example, a sulfite, such as sodium sulfite, potassium sulfite, ammonium sulfite, a thiosulfate, such as sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, etc.

[0013]

The color-changing fluid can be used mixed with a coloring agent. That is, the color-changing writing implement, such as a marker pen, etc., filled with color-changing fluid that contains the said sulfurous acid reducing agent, is used to trace over the written line, but a coloring agent can be filled in such implement when the color-changing fluid is filled in the said implement. When the implement filled with the color-changing fluid mixed with the coloring agent is used to trace over the written line, not only the initial written line changes color, but also the coloring agent filled additionally adds color for an enhancement effect.

[0014]

The coloring agent mixed with the color-changing fluid can be any coloring agent other than the basic dye erasable with a sulfurous acid reducing agent. Therefore, an acidic dye, direct dye, etc., or organic pigment or inorganic pigment, etc., can be used. Two or more of these can be used in combination. However, use of a coloring agent that is fainter than the discolored water-based ink of this invention is preferable.

[0015]

This invention is detailed further below with the aid of practical examples. Practical Examples 1-3 relate to the water-based ink and writing implement filled with the said ink of this invention.

Practical Example 1:

Table 1

{PRIVATE }ink material	(weight %)
C.I. Basic Red 13 (HODOGAYA KAGAKU KOGYO K.K. red basic dye)	5.0
C.I. Basic Blue 7 (HODOGAYA KAGAKU KOGYO K.K. blue basic dye)	5.0
ion-exchanged water	69.9
glycerol	20.0
DELTOP (tradename of antiseptic made by TAKEDA YAKUHIN KOGYO K.K.)	0.1

Material compounded at the above ratio is stirred into black water-based ink for ballpoint pens and thereafter the ink guiding polyester fiber core is assembled and a stainless steel tip is mounted, to produce a water-based ink ballpoint pen.

[0016]

Practical Example 2:

Table 2

{PRIVATE }ink material	(weight %)
C.I. Basic Green 1 (HODOGAYA KAGAKU KOGYO K.K. green basic dye)	3.0
C.I. Basic Orange 21 (HODOGAYA KAGAKU KOGYO K.K. orange basic dye)	1.0
C.I. Basic Red 1 (HODOGAYA KAGAKU KOGYO K.K. red basic dye)	1.5
ion-exchanged water	74.4
glycerol	20.0
DELTOP	0.1

The material compounded at the above ratio is stirred into black water-based ink for ballpoint pens. This water-based ink is filled in a polyester fiber cotton in a pen body similar to a normal commercial ballpoint pen (Be-109, ZEBRA K.K. trade mark) and thereafter the ink-guiding polyester fiber core is assembled and a stainless steel tip is mounted to produce a water-based ink ballpoint pen.

[0017]

Practical Example 3:

Table 3

{PRIVATE }ink material	(weight %)
C.I. Basic Blue 54 (HODOGAYA KAGAKU KOGYO K.K. blue basic dye)	8.0
Hostafine Yellow HR (Clariant-Japan K.K. orange pigment 35% aqueous dispersion)	15.0
ion-exchanged water	56.4
glycerol	20.0
xanthan gum	0.5
DELTOP	0.1

Material compounded as in Table 3 is stirred using a dissolver [sic] to obtain black gel ink for ballpoint pens. The viscosity of the produced gel ink was 110 mPa·s (25°C, shearing rate: 150 s^{-1}). The gel ink is filled in polypropylene refill, similarly to normal commercial gel-ink-type water-based ink ballpoint pens (ZEBRA BW-100, 0.7 mm stainless steel ball tip) and an ink follower is put in from the back part, is defoamed with 1960 $m \cdot s^{-2}$ (200 G) centrifugal force and this refill is put in the pen body to produce a gel-type water-based ink ballpoint pen.

[0018]

Comparison Example 1:

Table 4

{PRIVATE }ink material	(weight %)
C.I. Basic Red 1 (HODOGAYA KAGAKU KOGYO K.K. red basic dye)	4.0
C.I. Basic Blue 7 (HODOGAYA KAGAKU KOGYO K.K. blue basic dye)	3.0
C.I. Basic Yellow 21 (HODOGAYA KAGAKU KOGYO K.K. yellow basic dye)	3.0
ion-exchanged water	69.9
glycerol	20.0
DELTOP	0.1

The material compounded in Table 4 is stirred to obtain black water-based ink for marker pens. This ink is processed similar to Practical Example 1 to prepare a water-based ink marker pen.

[0019]

Below, Practical Examples 4 and 5 relate to a color-changing writing implement filled with color-changing fluid that changes color by tracing over the written line.

Practical Example 4:

Table 5

{PRIVATE }material of color-changing fluid	(weight %)
sodium sulfite	20.0
potassium carbonate	5.0
ion-exchanged water	74.9
DELTOP	0.1

The material compounded in Table 5 is stirred to obtain color-changing fluid. This fluid is filled in a polypropylene ink tank, similar to the normal direct fluid-type water-based ink marker pen (fluorescent Sparky-1, ZEBRA K.K. trade mark) and the valve and tip are mounted. A polyester fiber pen tip is mounted onto the said tip and the ink tank is kept at normal pressure to produce a color-changing writing implement. Here, the (color-changing writing implement) is a writing implement which can change the color of a written line written with the water-based ink of this invention by tracing over the said written line.

[0020]

Practical Example 5:

A color-changing writing implement with marking function was produced by using the same color-changing fluid of the above color-changing writing implement, except addition of 0.2 weight % of C.I. Basic Red 1 (BASF Japan K.K. red dye) and the ion-exchanged water was decreased by that much.

[0021]

Test Method:

The writing implements of Practical Examples 1-3 and Comparison Example 1 are used to handwrite on dry PPC paper (OJI SEISHI K.K. trademark) and the written lines are traced over with a color-changing writing implement and a color-changing writing implement with marking function (having a coloring agent for the marking function added to the color-changing fluid) of Practical Examples 4 and 5 to check the color change. The result is shown in Table 6.

Table 6:

{PRIVATE }	color of the written line	color of the written line after tracing over with a color-changing implement	color of the written line after tracing over with a color-changing implement with a marking function *
Practical Example 1	purple	blue	blue
Practical Example 2	black	red	red
Practical Example 3	black	orange	orange
Comparison Example 1	black	black	black

*In all cases, a yellow marking color was noted around the written line.

[0022]

As is clear in Table 6, a color change is evident when the line written with the water-based ink of this invention is traced over with a color-changing fluid that contains a sulfurous acid reducing agent, so that this color-changing function can be used to emphasize a specific part of the paragraph, etc. On the other hand, in the Comparison Example, a color change did not occur even after tracing-over with a color-changing writing implement with marking function and the original color of the written line remains.

[0023]

Effect of the invention:

As explained above, the written line of the water-based ink of this invention changes its color when it is traced over with a color-changing fluid that contains a sulfurous acid reducing agent, so that this color-changing function can be used to emphasize a specific part of a paragraph, etc. At such time, if the color-changing fluid is mixed with a coloring agent, the marking function of the said coloring agent is added to further emphasize the traced-over part.

Incidentally, with the writing implement of this invention, filled with the water-based ink of this invention, the implements need not be switched, even if the color of the written line needs to be changed, nor the written line need not be erased, therefore time and work can be saved.

Especially, if the water-based ink is a dark color and the color after color change is relatively faint, only the color-changed part is erased when the written line is partially color-changed, so that when a semitransparent sheet of the same color as the color-changed color is placed over the color-changed written line, this can be used for memory retention, etc., and a new learning method can be offered.

Continuation of front page:

F-term (ref.): **2C350 GA03 GA04 NA18 NA19**
4J039 BA06 BA13 BA18 BA20 BA35
BC39 BC50 BC53 BC60 BC69
BE01 BE05 BE33 CA03 CA06
EA29 GA26 GA27